

## **WASH SOLUTION BATH LIFE EXTENSION FOR THE SPACE SHUTTLE ROCKET MOTOR AQUEOUS CLEANING SYSTEM**

by

Chad Saunders  
Kurt Evans  
Neil Sagers

Thiokol Propulsion  
P.O. Box 707 - M/S 245  
Brigham City, UT 84302

### **ABSTRACT**

A spray-in-air aqueous cleaning system, which replaced 1,1,1 trichloroethane (TCA) vapor degreasing, is used for critical cleaning of Space Shuttle Redesigned Solid Rocket Motor (RSRM) metal parts. Small-scale testing demonstrated that the alkaline-based wash solution possesses adequate soil loading and cleaning properties. However, full-scale testing exhibited unexpected depletion of some primary components of the wash solution. Specifically, there was a significant decrease in the concentration of sodium metasilicate which forced change-out of the wash solution after eight days. Extension of wash solution bath life was necessary to ease the burden of frequent change-out on manufacturing. A laboratory study supports a depletion mechanism that is initiated by the hydrolysis of sodium tripolyphosphate (STPP) lowering the pH of the solution. The decrease in pH causes polymerization and subsequent precipitation of sodium metasilicate (SM). Further investigation showed that maintaining the pH was the key to preventing the precipitation of the sodium metasilicate. Implementation to the full scale operation demonstrated that periodic additions of potassium hydroxide (KOH) extended the useful bath life to more than four months.

### **INTRODUCTION**

The Thiokol Corporation Clearfield Utah facility refurbishes reusable post flight Space Shuttle solid rocket motor metal hardware. Several processes are employed to strip the paint, insulation, and charred material down to a virgin metal surface. After refurbishment, the hardware is shipped 75 miles north by rail to the primary manufacturing area and undergoes a final surface preparation process (aqueous clean and grit blast) prior to bond assembly. Previously, TCA vapor degreasing was used to clean the metal surface at both locations. Recently, aqueous cleaning replaced vapor degreasing because of the ozone depleting properties of TCA. The aqueous cleaning process, which consists of three phases (wash, rinse 1, and rinse 2) is conducted in a Proceco Incorporated spray-in-air system. Sub-scale testing was used to optimize process parameters which included determination of the ideal concentration and temperature of the cleaner.

The full-scale process demonstrated a 20°F reduction in wash solution temperature after circulation from the heated holding tank to the spray in air nozzle. This reduction compromised cleaning efficiency and increased foaming in the cleaning chamber. Apparently, the foam suppression mechanism of the nonionic surfactants was inadequate at the lower temperature. The wash solution set temperature was increased from 150 to 170°F to compensate for the heat loss.

Analysis of the cleaning solution showed depletion of several primary components of the alkaline cleaner. Specifically, the rate of depletion of SM and STPP was greater than initially predicted. This depletion was unacceptable because violation of concentration-based acceptance limits for the primary components of the alkaline cleaner were established to ensure the cleanliness and condition of the hardware. Violation of these limits burdens manufacturing operations with frequent change-out of the wash solution. cursory review of the chemistry data linked the depletion of STPP to the increase in wash solution temperature from 150 to 170°F and localized heating in excess of 170°F in the heating tank.

A laboratory study confirmed that the depletion of STPP is dependent upon the temperature of the wash solution. It also determined that STPP depletion reduces pH which jeopardizes the SM solubility which is a function of pH. A subsequent laboratory study demonstrated that additions of potassium hydroxide (KOH) to the wash solution controls pH above levels which circumvent SM precipitation, thereby extending the useful bath life of the wash solution. This KOH add-back method was successfully demonstrated in the full-scale system through a bath life study which extended the bath life to at least 120 days.

## **RESULTS AND DISCUSSION OF THE TEMPERATURE STUDY**

The objective of this study was to determine the effect of exposure of the wash solution to a range of production representative temperatures on the pH and cleaner constituent concentrations.

### **General Outline of Procedure**

Three distillation apparatuses were configured to maintain 10-percent solutions of the alkaline cleaner at temperatures of 150°F, 175°F and 200°F for five twenty-hour cycles. The three temperatures replicated the range of temperatures of the wash solution in the full-scale production process. General observations of the physical state of the solutions were recorded throughout cycling. At the end of each 20-hour cycle an aliquot of the solution was removed and the primary components of the cleaner were determined for these samples. The following table lists the primary components of the cleaner (excluding water and potassium hydroxide) and the analytical techniques used for measurement. Alkalinity and pH were also determined.

**Table 1. Analytical Methods**

<b>Alkaline Cleaner Component</b>	<b>Method of Analysis</b>
Sodium Tripolyphosphate	Ion Chromatography
Sodium Metasilicate	ICP-AES UV/Vis Colorimetric
D-08 (Anionic Detergent)	HPLC
D-22 (Anionic Detergent)	HPLC
D-26 (Nonionic Detergent)	HPLC
D-30 (Nonionic Detergent)	HPLC

Sixteen samples were collected during the study. The samples consisted of one control of the initial cleaner solution and 15 samples collected from five intervals of 20 hours for three temperatures (150°F, 175°F and 200°F). A cycle refers to the heating of a sample from ambient to the controlled temperature (150°F, 175°F, or 200°F) maintaining the sample at that temperature for 20 hours, then cooling back to ambient temperature. No external cooling was applied. A reference to "Cycle 3" indicates that the sample was collected after the third cycle and was exposed to the controlled temperature for a total of 60 hours. A 20-hour cycle simulated the time duration to complete a single production wash cycle if the cleaning solution is initially at ambient temperature.

Figures 1, 2 and 3 illustrate the behavior of the cleaner components during cycling at each temperature in terms of percent of initial concentration. In figure 3, the last three data points for D-30 were not included because the actual concentration was lower than the detection limit of the method. The relative detection limit is 40 percent of the initial concentration. The concentration of the each component at time zero was determined from the control sample.

The plots show that temperature significantly affects the concentrations of STPP, SM and pH. The effect on the surfactants is less marked except at 200°F. A more detailed discussion of the effect of temperature on each cleaner constituent follows.

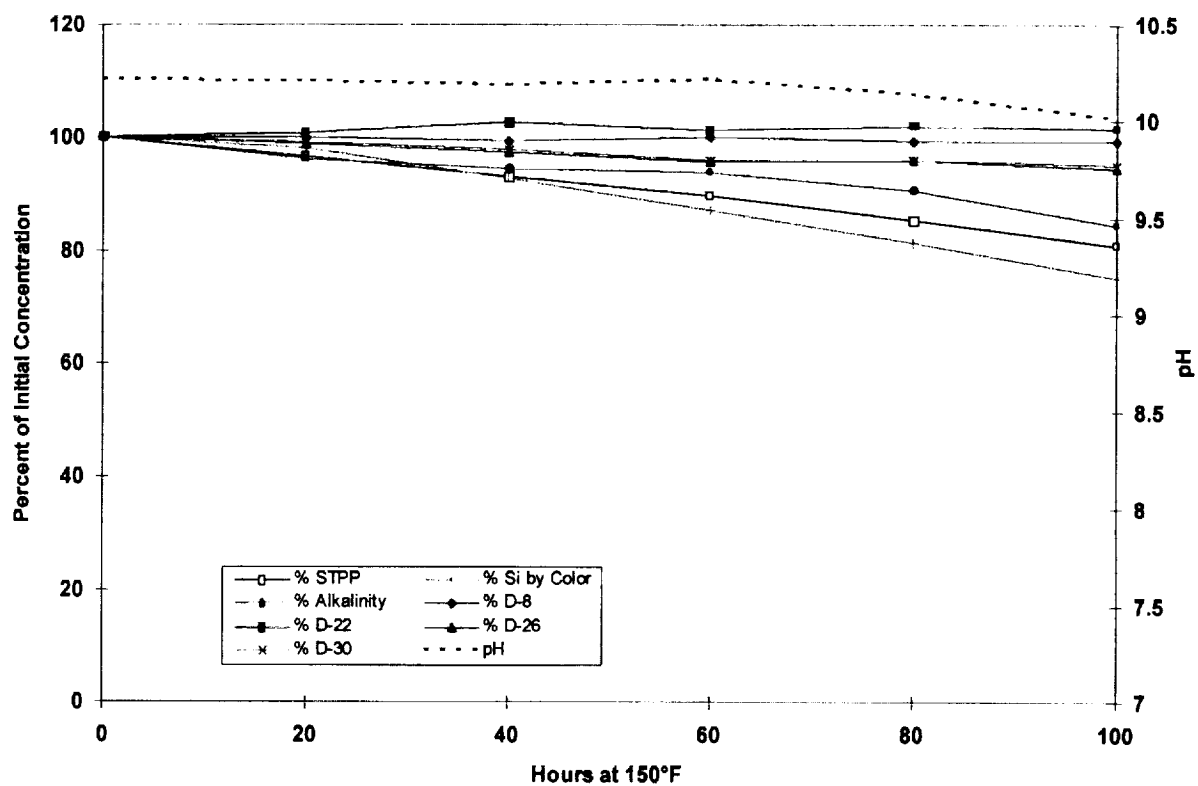


Figure 1. Percent Depletion of All Components at 150°F

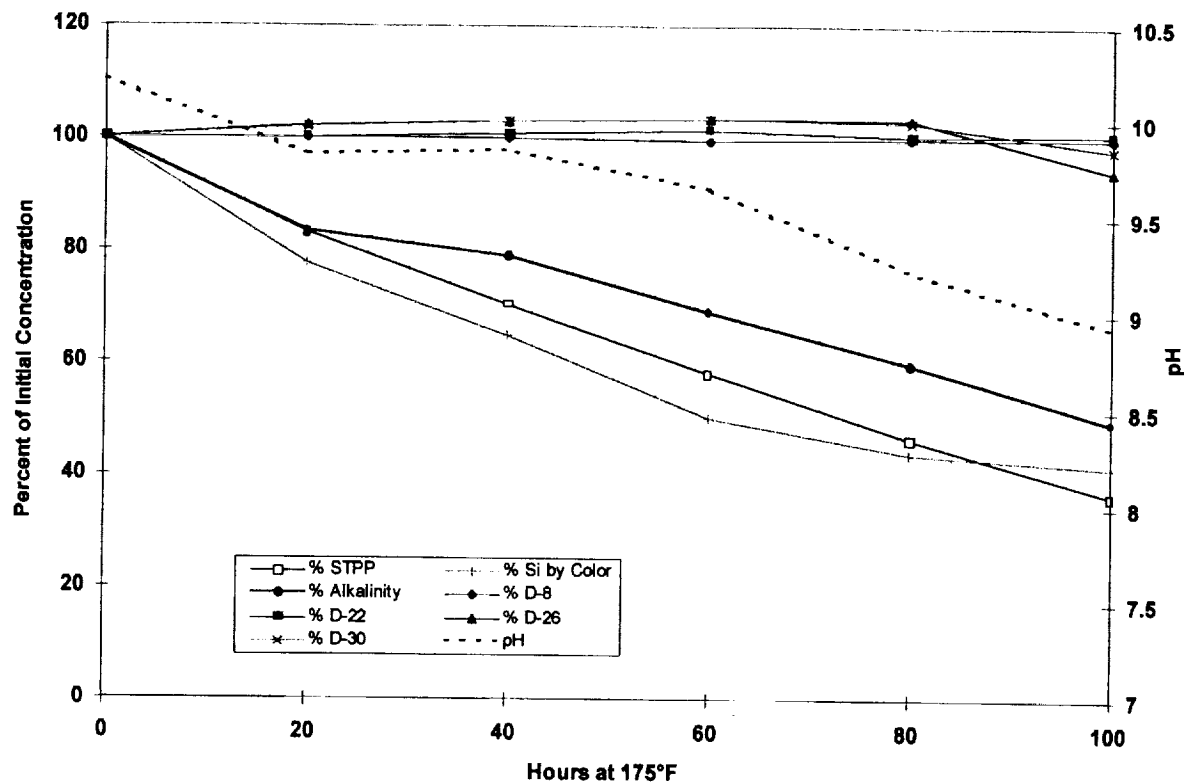


Figure 2. Percent Depletion of All Components at 175°F

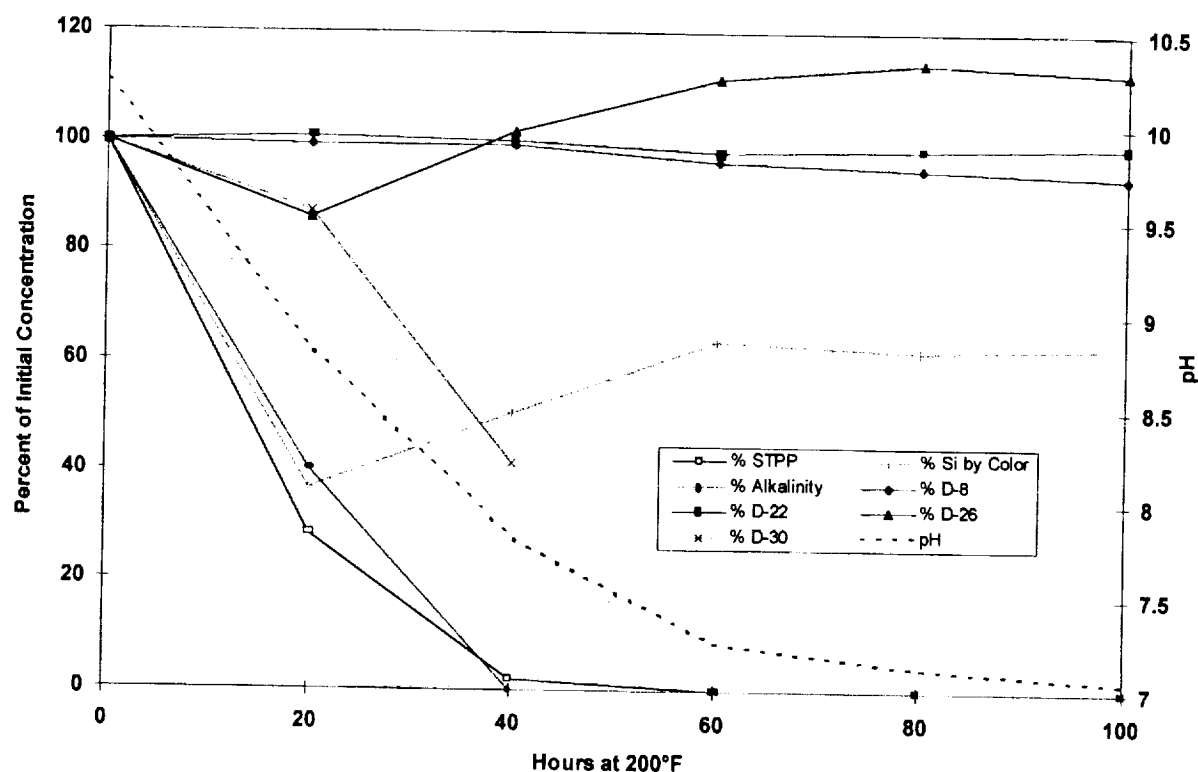


Figure 3. Percent Depletion of All Components at 200°F

### Sodium Tripolyphosphate (STPP)

Sodium tripolyphosphate (STPP) functions as a builder in the alkaline cleaner. Builders are added to cleaners to sequester water-soluble polyvalent ions (alkaline earth and transition metals) and prevent them from interfering with detergents in the cleaner. In addition, STPP deflocculates dirt particles and contributes to the alkaline buffer capacity<sup>(1)</sup>. Tripolyphosphate ( $P_3O_{10}^{5-}$ ) is the linear form of triple condensed orthophosphate. Depletion of STPP occurs when a tripolyphosphate molecule is hydrolyzed to form one molecule of orthophosphate ( $PO_4^{3-}$ ) and one molecule of pyrophosphate ( $P_2O_7^{4-}$ ). Further hydrolysis of the pyrophosphate results in two molecules of orthophosphate<sup>(2)</sup>. Figure 4 shows the concentration of STPP and its hydrolysis products over time at the three temperatures as a percentage of the molar phosphorous concentration.

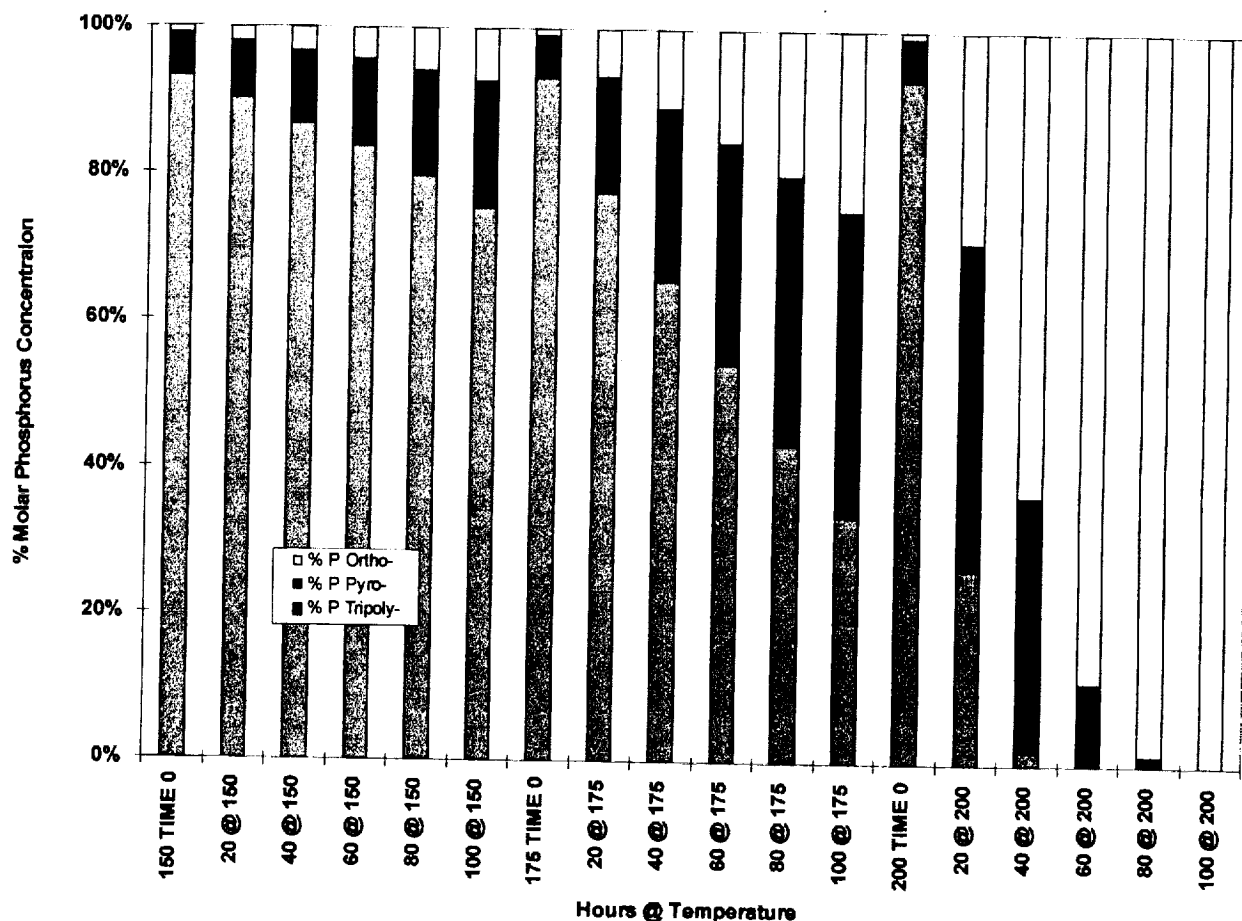


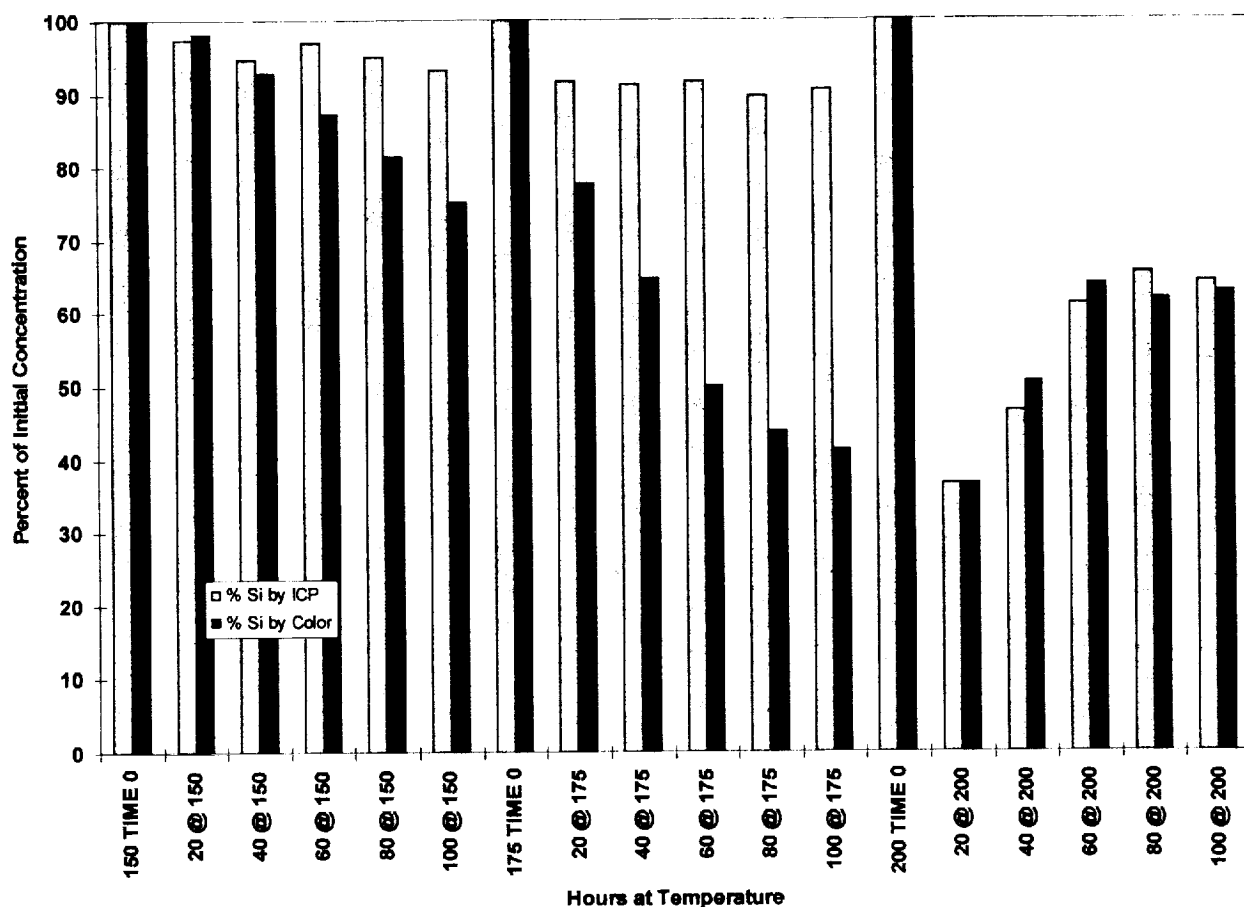
Figure 4. Speciation of Phosphates at 150, 175 and 200°F

This figure illustrates the effect temperature has on the hydrolysis rate of STPP. The magnitude of this effect, particularly at 200°F, supports the theory that localized intense heat from the heat source can significantly accelerate the loss of STPP from cleaning solutions.

#### Sodium Metasilicate (SM)

Sodium metasilicate functions as a corrosion inhibitor, deflocculant, and wetting agent. Figure 5 compares the silicon results from ICP-AES and UV/Vis colorimetric analysis (heteropolyblue silicomolybdic complex) of the samples collected during the temperature cycle study. A significant difference is observed between the silicon results obtained by the two procedures. This discrepancy can be attributed to sensitivity differences of the two procedures for various silicon species. (A literature search is in progress to determine the silicate forms for which the colorimetric method is sensitive. )

The results suggest that the colorimetric method is less sensitive to the polymeric silicates than the ICP-AES method. The latter method detects any form of soluble silicon that is aspirated into the plasma.



**Figure 5. Metasilicate at 150, 175 and 200°F**

It has been determined experimentally that the metasilicate monomer is the dominant species at a pH greater than 10.9. However, longer silicate polymers, colloids, and possibly crystalloids are formed when the pH is lower<sup>(3)</sup>. Figures 2 and 3 show a steady decline in pH. Figure 5 shows a significant difference in metasilicate concentration measured by the two analytical techniques at 175°F. Apparently, at this temperature the pH is decreasing at a rate slow enough to observe the formation of longer, soluble silicate polymers. The rate in the decline of pH is much faster at 200°F than 175°F. At 200°F, an insoluble silicate residue was collected from each of the samples and the results of ICP-AES and colorimetric analysis are essentially the same.



### **Alkalinity and pH**

Alkalinity is a measurement of the buffer capacity of the solution to accept free acid. The performance of most aqueous cleaners is optimal under alkaline conditions and over a limited range in pH. In addition, ferrous surfaces are less susceptible to corrosion in an alkaline environment. It should be noted that the method for determining alkalinity in this study is a direct titration method to an end point near a pH of 7. Typically, measurement of free alkalinity provides meaningful data concerning the buffer capacity of a solution to accept  $H^+$ . Tripolyphosphate is the component of this alkaline cleaner that serves as a buffer over the useful pH range. It is difficult to establish appropriate acceptance values for free alkalinity because the buffering capacity of the wash solution is continuously shifting as the STPP is hydrolyzed. Thus, free alkalinity monitoring is less meaningful to this aqueous cleaning solution.

### **Anionic and Nonionic Detergents**

The alkaline cleaner contains four surfactants. D-8 and D-22 are the numerical references assigned to the anionic surfactants and D-26 and D-30 refer to the nonionic surfactants. The actual names and composition of the surfactants are proprietary. The production database indicates that the surfactant concentrations remain relatively constant throughout hardware cleaning. The temperature cycle study verifies that the surfactants are thermally stable. This is particularly true of the anionic surfactants which showed no decomposition at any of the temperatures. Figures 1, 2 and 3 illustrate the concentration behaviors of the surfactants over time at the tested range of temperatures. These charts also show that D-26 and D-30 were stable at 150°F and 175°F. However, at 200°F the concentration of D-30 decreased below detectable levels and D-26 increases in concentration. Size exclusion chromatography was the method used to monitor the concentration of D-26 and D-30 and it is possible that a converted form of D-30 is being detected as D-26 by this technique.

### **Conclusions of Temperature Study**

The temperature study presented herein is an attempt to understand the reason for depletion of primary components of Brulin 1990 GD during the acceptance limit testing. A great deal of information has been gained by monitoring the individual components after exposure to elevated temperature. The temperature study strongly supports our suspicion that increasing the temperature of the aqueous cleaning solution does accelerate the depletion of the STPP and metasilicate. In addition, the pH of the solution decreases as a function of temperature and may have a role in depletion of the key components as well. The information gained during the temperature study will be used to direct a literature search to determine possible mechanisms for depletion.

## INTRODUCTION OF DEPLETION MECHANISM

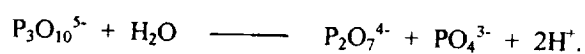
The results of the temperature study were reviewed in conjunction with full-scale production data. This review revealed four factors that limit useful bath life of the production system wash solution.

The first factor relates to the instability of all components at the extreme temperature of 200°F. The wash solution is exposed to this temperature because of localized heating in the area near the steam heated coils in the holding tank. To circumvent this problem, a circulating pump was installed in the holding tank to reduce pockets of intense heat and eliminate the heating gradient.

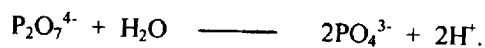
The remaining three factors were the decrease in the nominal concentration of metasilicate, pH and tripolyphosphate. The decrease in the concentration of the three components was observed at varying degrees at all three temperatures. The depletion of the SM is the most significant because the concentration fell below established production acceptance limits in approximately eight days.

The information from the temperature study was combined with additional information obtained from literature sources to develop a correlation between STPP hydrolysis and the depletion of other components. In 1984, a kinetic study on the hydrolysis of tripolyphosphate was performed at the University of Zurich. The study described the effect that pH and temperature have upon the reaction and showed that the highest reaction rates occur at low pH and high temperature.<sup>(2)</sup> The hydrolysis reaction of tripolyphosphate and pyrophosphate occurs as follows:

Hydrolysis of tripolyphosphate,



Hydrolysis of pyrophosphate,



Both hydrolysis reactions liberate free acid as products. Figures 1, 2 and 3 show that both alkalinity and pH decrease as a function of temperature. The decrease of both parameters correlates closely with the liberation of acid that occurs when tripolyphosphate decomposes to orthophosphate. Identification of the hydrolysis of tripolyphosphate as a source of acid was an important breakthrough. Previously, it was hypothesized that the decrease in solution pH was caused by absorption of atmospheric carbon dioxide. However, the wash solution is enclosed in a holding tank which limits atmospheric exposure. Thus, the hydrolysis of tripolyphosphate is the probable mechanism responsible for decreasing wash solution pH.

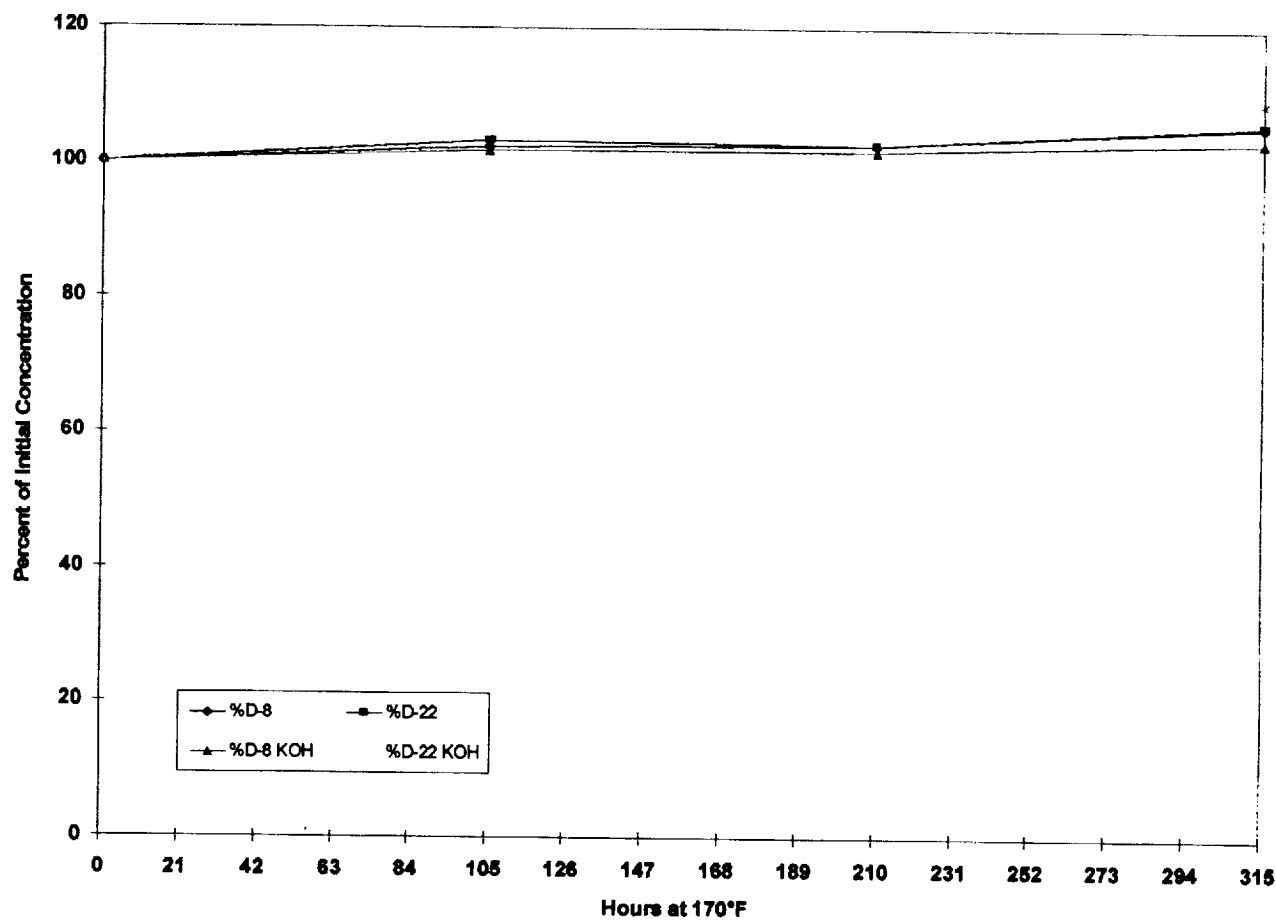
Further research indicated that metasilicate depletion is indirectly caused by the elevated temperature. This mechanism is more a function of wash solution pH. According to technical references, soluble silicates polymerize in solution until the polymer exceeds solubility causing the formation of colloids and crystalloids. The extent of polymerization is greatly influenced by the pH of the solution<sup>(3)</sup>.

In summary, the depletion mechanism as derived from both the literature and data collected in the temperature study supports the theory that the rate of STPP decomposition is a function of temperature. The decomposition of STPP is a hydrolysis reaction that liberates free acid and subsequently lowers the pH of the solution. The polymerization of sodium metasilicate increases as the pH of the cleaning solution drops. Eventually, the propagation of the silicate polymer exceeds the solubility limit and a residue is observed.

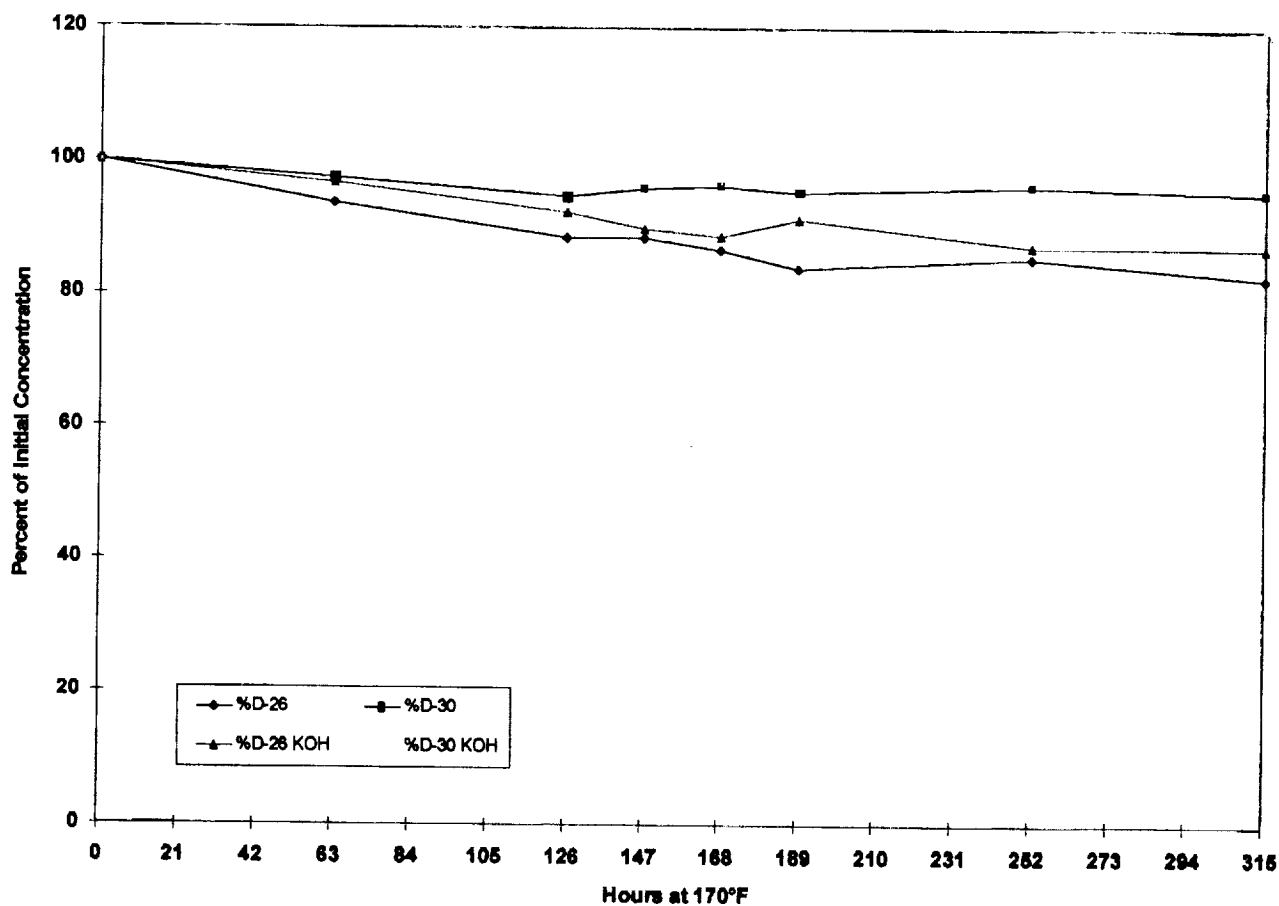
Identification of the depletion mechanism permitted the conception of an approach to extend the useful bath life of the wash solution. A key element to this approach is to maintain the pH of the wash solution above the critical level at which metasilicate precipitates. This objective can be accomplished simply by adding KOH, a primary constituent of the cleaner, to the wash solution. This approach does not prevent STPP depletion. This is acceptable because the sequestering action is mitigated by use of deionized water in the wash solution. (The possibility of reduction of the wash solution process temperature was considered. However, this approach is impractical because of foaming, cleaning efficiency and system requalification issues.)

## **RESULTS AND DISCUSSION OF KOH ADD BACK STUDY**

A second study was designed to investigate the effect of periodic additions of potassium hydroxide (KOH) to adjust the pH of the solution back to its nominal value. Two distillation apparatuses were configured similar to that of the temperature study. The alkaline cleaner solutions were maintained at 170°F for 21 hours cycles. At the end of each 21-hour cycle the KOH was used to adjust the pH of one of the solutions back to its nominal value of 10.3. The other solution was used as a control and left unchanged. The study was extended to 15 cycles for a total of 315 hours so that the precipitation of the metasilicate could be observed in the control sample. Samples collected at the end of each 21-hour cycle were analyzed by using the methods listed in Table 1. The following figures show the results of this study.

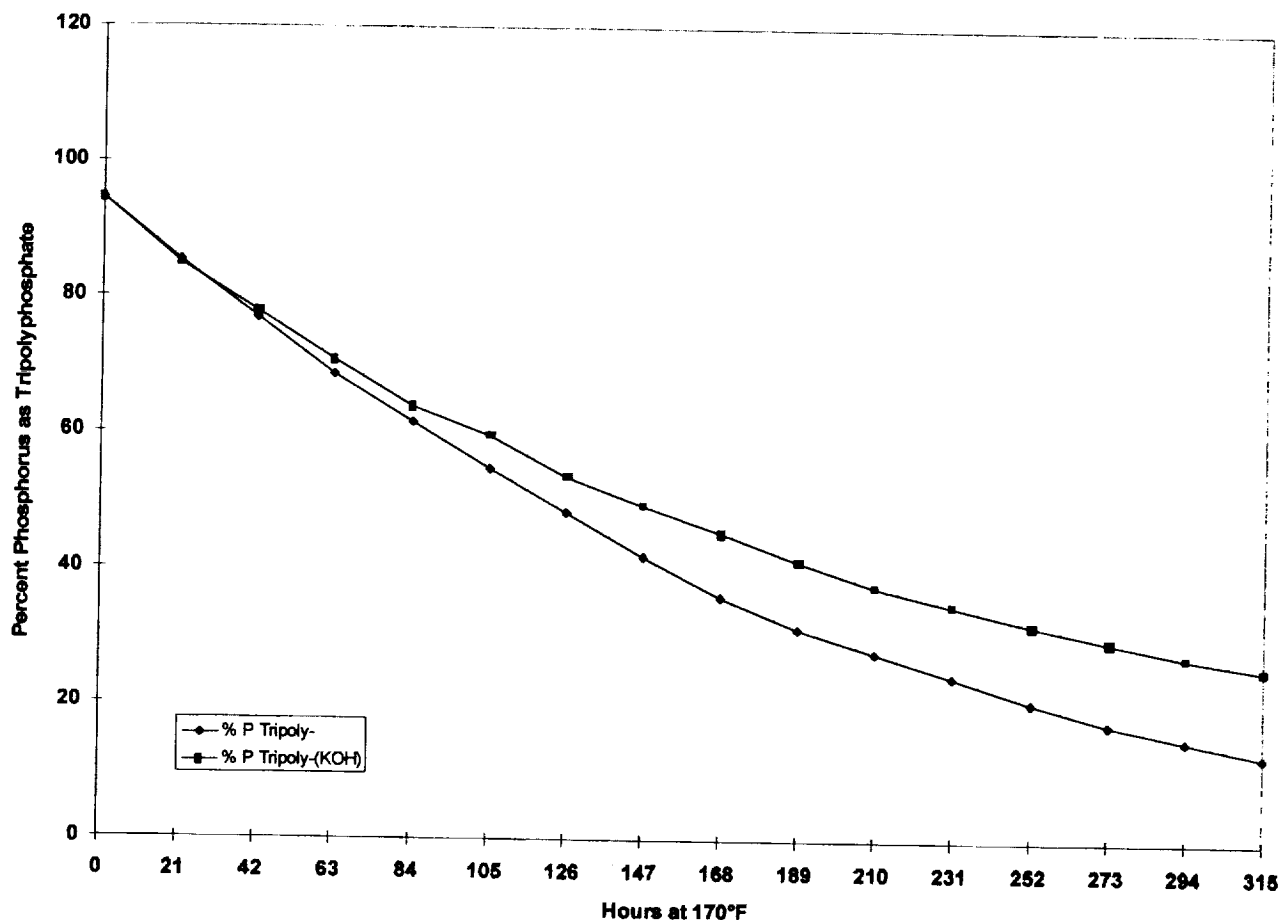


**Figure 6. Anionic Surfactants at 170°F**



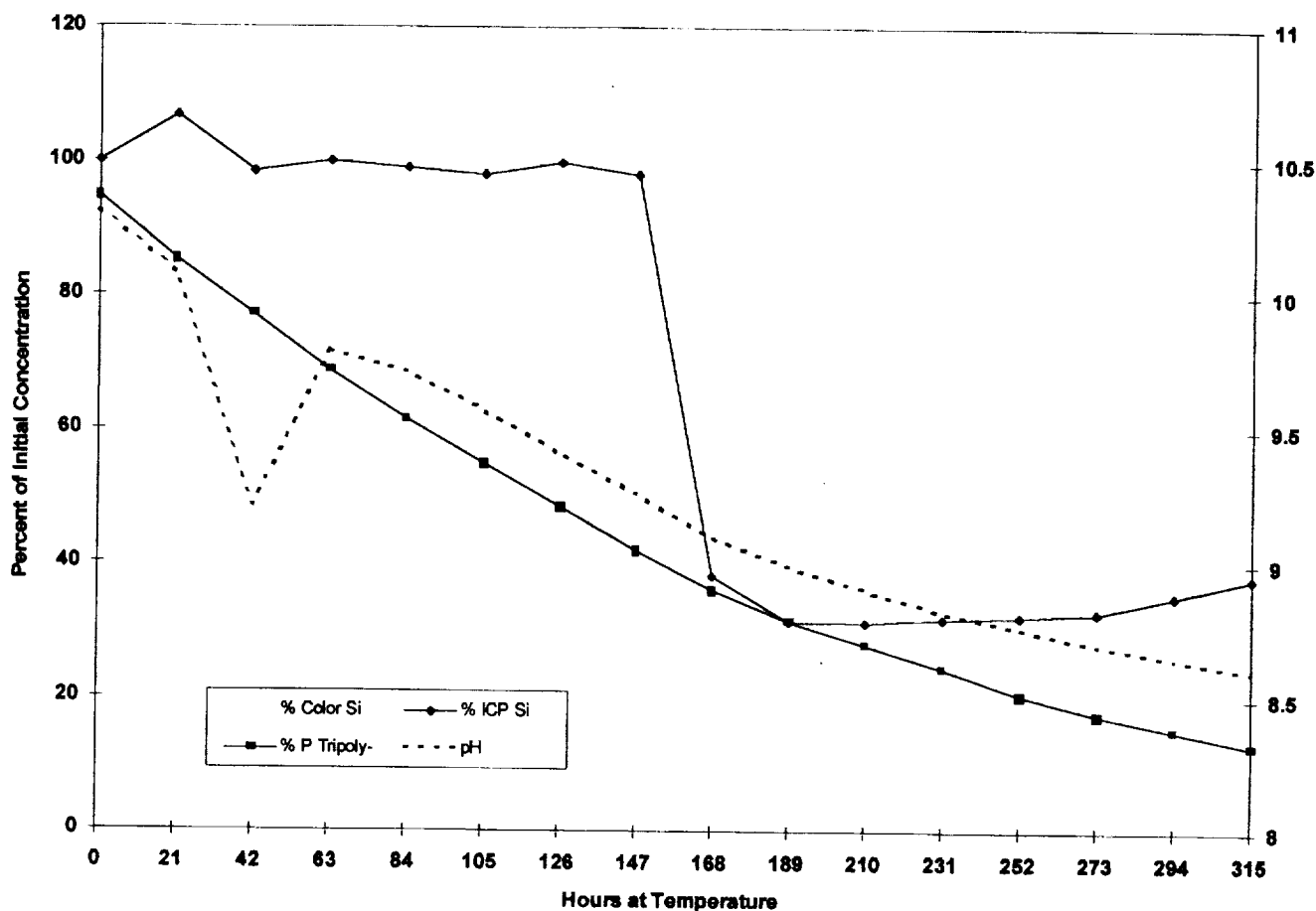
**Figure 7. Nonionic Surfactants at 170°F**

Figures 6 and 7 show that both the concentration of the anionic and nonionic surfactants are relatively stable and independent of additions of KOH. The surfactant package tolerates variation in temperature and pH by exhibiting exceptional soil loading and cleaning efficiency characteristics throughout sub- and full-scale testing.



**Figure 8. Sodium Tripolyphosphate at 170°F**

The literature which discusses the hydrolysis of STPP states that lower solution pH accelerates the depletion of STPP. Therefore, it was anticipated that a cleaner solution with controlled pH would sustain a higher concentration of STPP than the uncontrolled solution. This outcome is exhibited in Figure 8. At zero time, both solutions measured an identical pH of 10.30. However, as the hydrolysis reaction liberated free acid, the pH of the solutions dropped. The pH of the solution with KOH additions was maintained at  $10 \pm 0.3$ . Conversely, the control solution pH decreased from 10.3 to 8.6 over the duration of the study. After 315 hours at 170°F, the solution with KOH additions was approximately twice the concentration of STPP as the control sample.



**Figure 9. Aqueous Cleaner Chemistry without pH Maintained**

The format of Figures 9 and 10 differs from the previous three charts. The SM concentration results of the KOH add back solution are presented separately from that of the control sample. This change allows for plotting and discussion of the effect of the STPP hydrolysis reaction on all other components. Figure 9 graphs the depletion of SM, pH and STPP as function of time at 170°F. The depletion of pH and SM is initiated by the hydrolysis of STPP which depletes to less than twenty percent of its initial concentration and liberates acid as a product of the reaction. The liberated acid causes the pH of the solution to decrease from 10.3 to 8.6 over the course of the study.

The extent of polymerization of the metasilicate as determined by the colorimetric method coincides with the decrease in pH. It is interesting to note that the deviation in pH and colorimetric results at 42 hours occurred because the sample container became unsealed which allowed interaction with atmospheric carbon dioxide. The carbon dioxide absorbed into the solution, reduced the pH, and caused the metasilicate to polymerize.

This event occurred while the sample was stored at 4°C. Two sets of metasilicate results are included in Figure 9 so that the polymerization of metasilicate can be observed. The colorimetric method is most sensitive for the monomer of metasilicate. The ICP method determines all forms of silicate except for the insoluble portion. The two methods are useful to distinguish the form in which the metasilicate is present in the solution. Initially the pH of the solution is high and favors conditions for the metasilicate monomer. As the pH is lowered by the hydrolysis of tripolyphosphate the metasilicate monomers form to soluble oligomers and polymers which is shown in Figure 9 by the decline in the data as determined using the colorimetric method. However, the soluble silicon element concentration remain unchanged until the pH of the solution decreases to 9.2 as indicated by the data obtained from the ICP method. Below this pH the concentration of the soluble silicates declines to 40-percent of the initial concentration and a precipitate of insoluble silicates is observed.

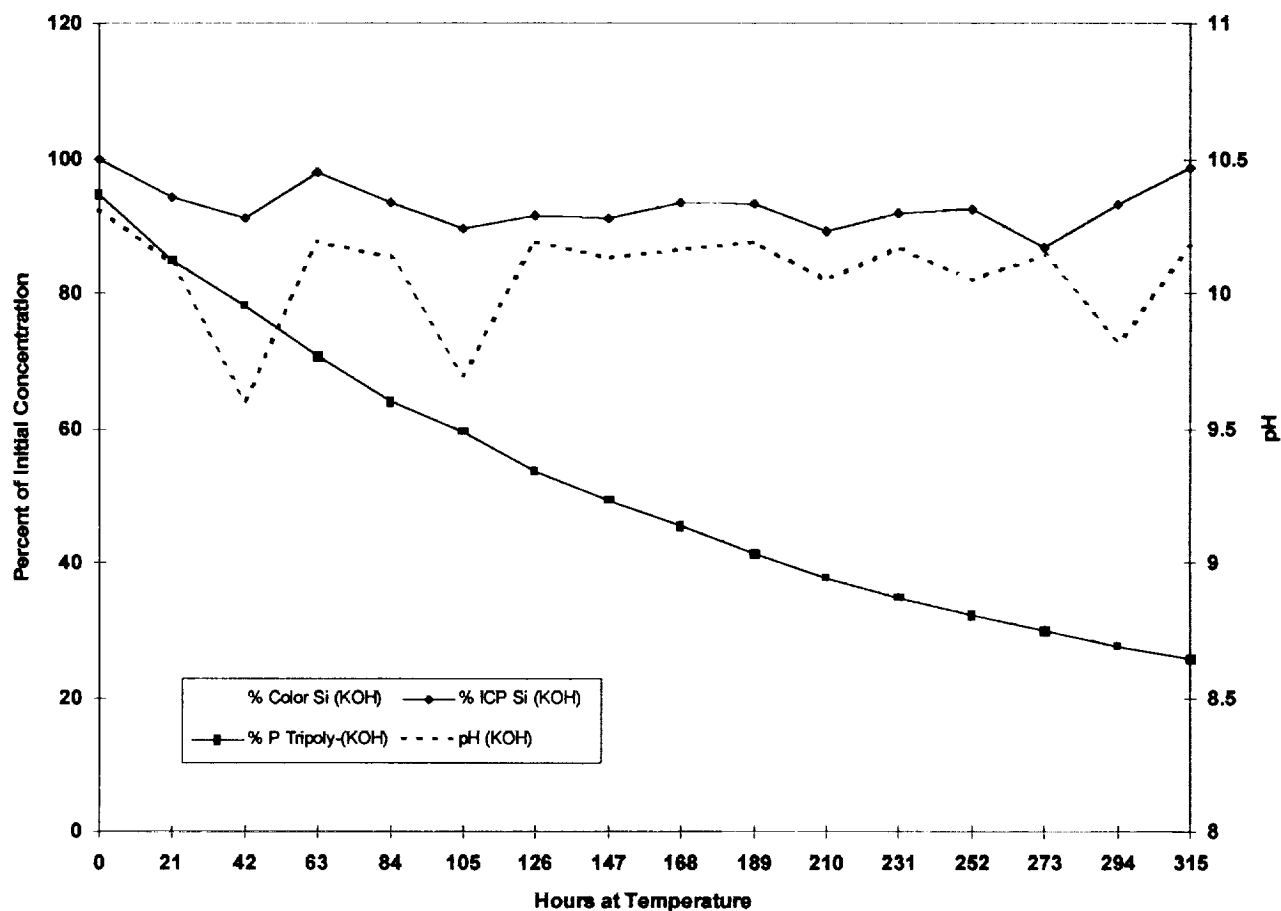


Figure 10. Aqueous Cleaner Chemistry with pH Maintained



### **Conclusions of the KOH Add Back Study**

The results of this study confirm the theory that the rate of STPP decomposition increases significantly as a function of temperature. The decomposition of STPP is a hydrolysis reaction that liberates free acid and consequently lowers the pH of the solution. The polymerization of SM increases as the pH of the cleaning solution drops. Eventually, the propagation of the silicate polymer exceeds the solubility limit and a residue is observed. The pH and SM concentrations of the cleaning solution can be controlled by addition of KOH.

### **PRODUCTION IMPLEMENTATION OF THE KOH ADD BACK METHOD**

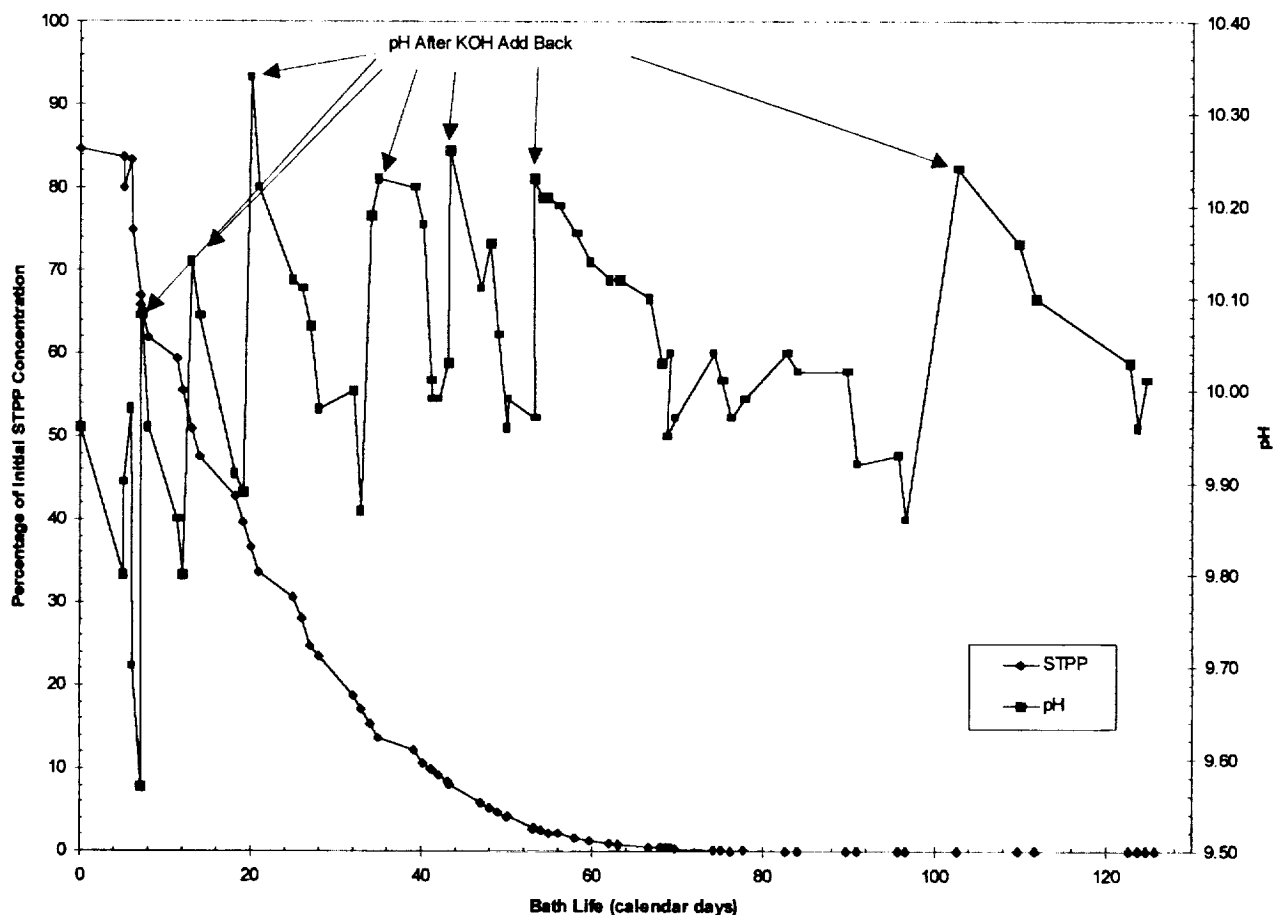
The KOH add back method was recommended to the production process to control wash solution pH and SM concentrations. The effectiveness of the method was assessed in the full-scale system through a bath life study which transpired over about 125 days. (Testing was terminated to accommodate production implementation of this aqueous cleaning system.) To strengthen the KOH add back database, numerous full-scale production components were washed and rinsed throughout the study. KOH was added to this 2,200 gallon system eight times for a total of 14,230 gram (31.4 pounds). The add back events are correlated to pH in Figure 11.

To verify the cleaning efficiency of KOH adjusted wash solution, bond testing was conducted on a weekly basis. Bond specimen test cycles consisted of fracture energy (tapered double cantilever beam) samples which simulate production bondlines (aluminum/EA 913NA adhesive and steel/EA 913NA adhesive). These samples are extremely sensitive to surface blemishes such as contamination caused by inefficient cleaning or rinsing.

### **pH Chemistry**

Figure 11 plots the pH and STPP concentrations of the wash solution over the life of the bath during this study. Figure 11 also relates KOH addition events to pH. The KOH add back method effectively controlled the wash solution pH above the critical level (9.3) required to prevent SM precipitation. As expected, the frequency of KOH addition corresponded to pH fluctuation. Six of the seven additions occurred before 55 days of bath life during the period of greatest fluctuation in pH. Approximately 50 days elapsed between the sixth and seventh/final additions. The period of greatest pH fluctuation also corresponded to the interval of exponential rate of STPP depletion. Eventually, the pH stabilized as the STPP concentration approached zero. Any pH fluctuation subsequent to complete depletion of STPP was attributed the decomposition of pyrophosphate which also liberates free acid but at a slower rate than the tripolyphosphate.

Figure 11 also identifies the time to depletion of the STPP concentration below the production process parameter control limit. In effect, this rate limits the wash solution bath life to about 30 days under the present process control protocol. The bath life could be increased to about 120 days if the process control protocol excluded the STPP concentration limit.



**Figure 11. STPP Concentration and pH versus Full-Scale System Bath Life**

### Phosphate Chemistry

Figure 12 correlates the phosphate concentration data to the wash solution bath life. The hydrolysis reaction is exhibited in the behavior of the phosphate constituents in the wash solution. The STPP concentration depleted to an undetectable level (<3.3 ppm) after about 76 days.

Simultaneously, the sodium orthophosphate and pyrophosphate concentrations increased until about 55 days. Thereafter, the hydrolysis of pyrophosphate becomes the primary source of additional orthophosphate. The hydrolysis of pyrophosphate had not gone to completion when testing was terminated.

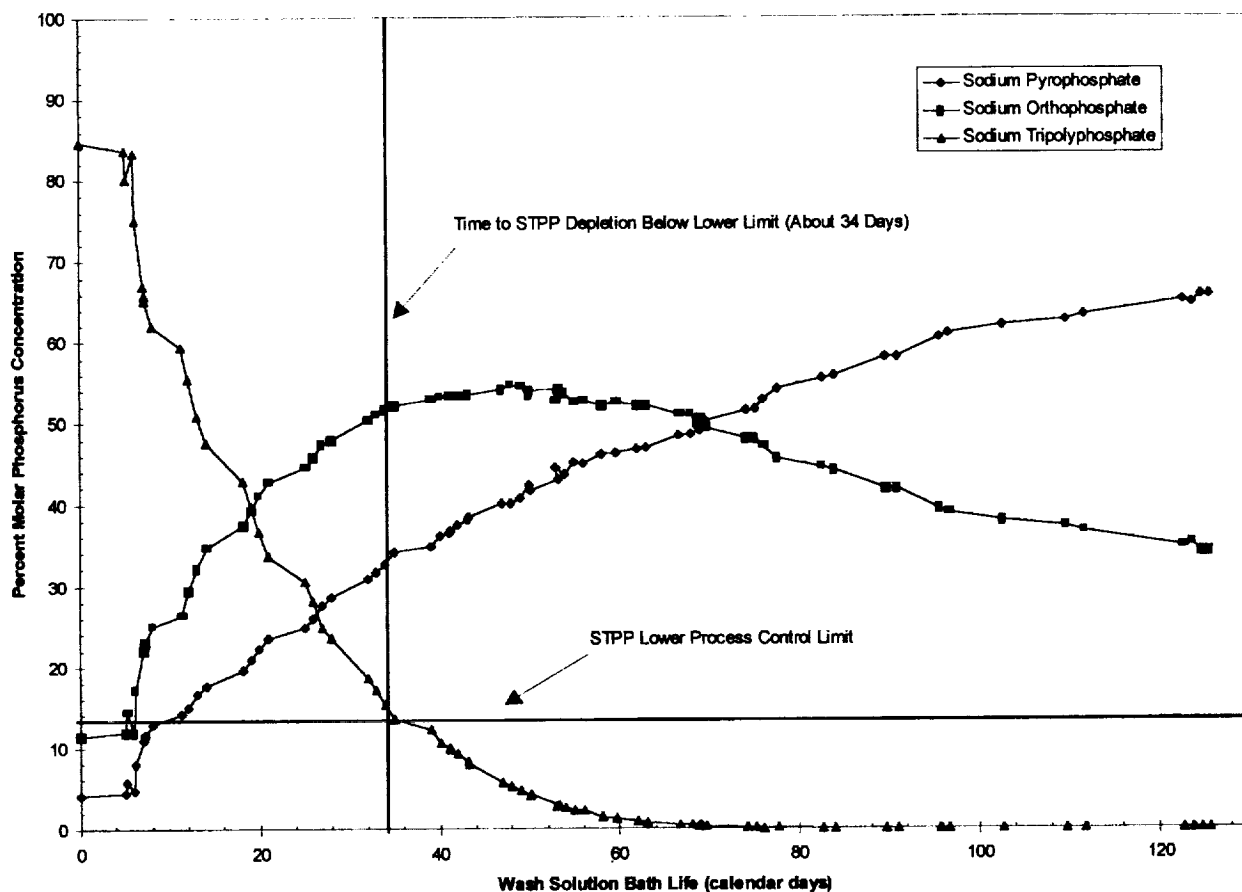


Figure 12. Phosphate Concentrations versus Full-Scale System Bath Life

### Elemental Concentrations

The elemental concentration analyses are plotted in Figure 13. These concentrations are indicators of components of the alkaline cleaner of which they are elemental constituents.

Specifically:

- Silicon (Si) is a constituent of SM
- Sodium (Na) is a constituent of SM, STPP, and the anionic surfactants
- Phosphorous (P) is a constituent of the phosphates
- Potassium (K) is a constituent of KOH

The Na and P elemental concentrations remained constant in the wash solution over the life of the bath.

Predictably, the K concentration increased over time because of KOH additions. The Si concentration also increased overall. This outcome is not well understood. A plausible explanation is the reintroduction into solution of sodium metasilicate contained in preexisting tank residues through pH manipulation.

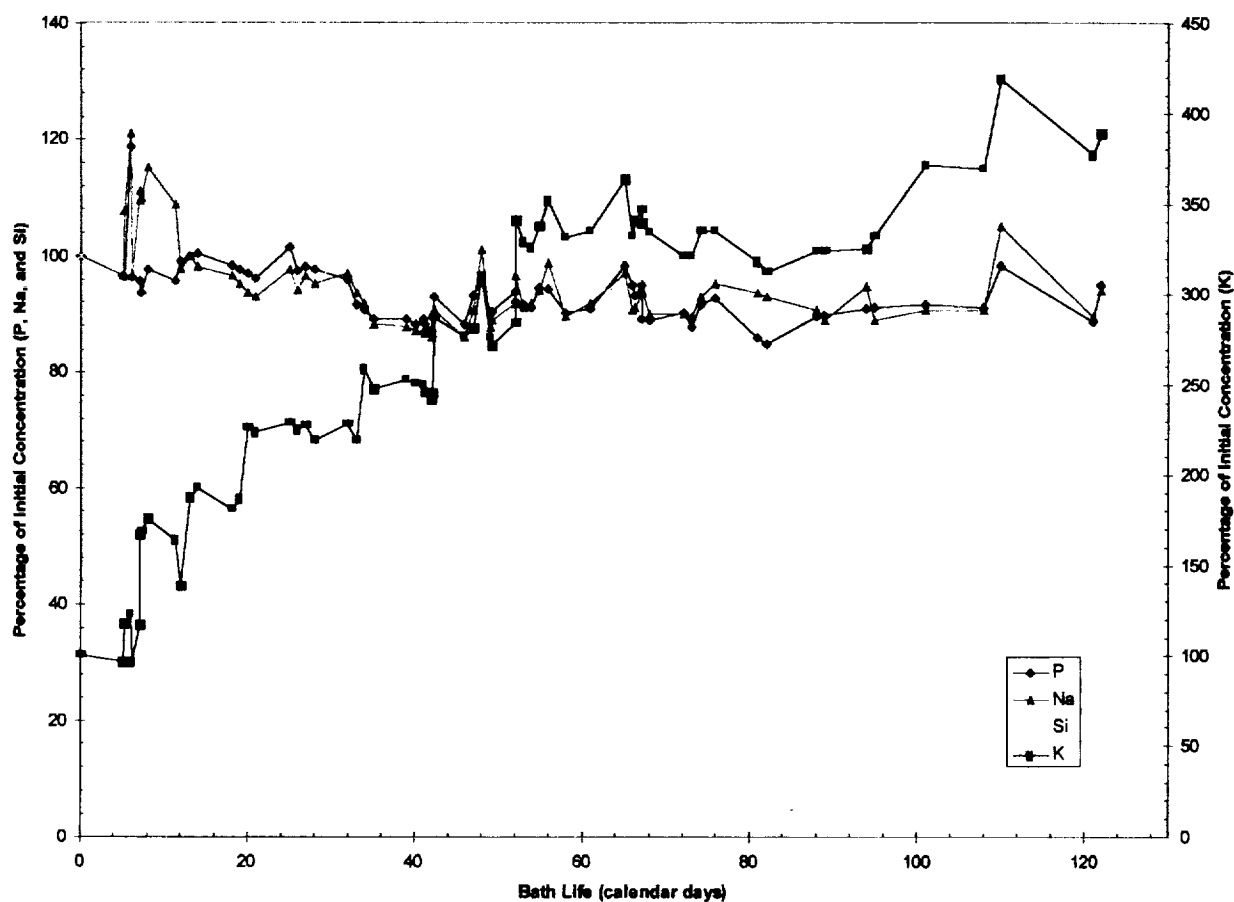
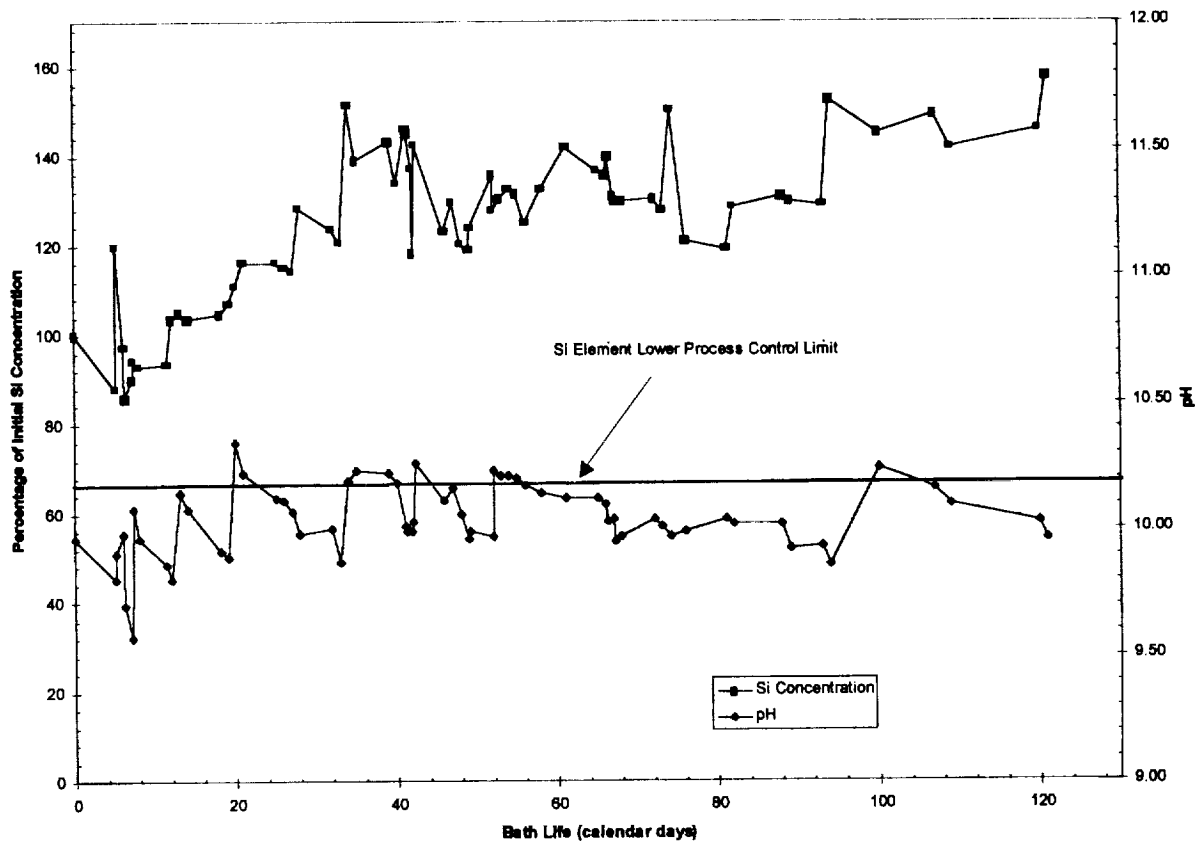


Figure 13. Elemental Concentrations versus Full-Scale System Bath Life

Figure 14 plots another relevant relationship, pH and Si element concentration vs. time. Early in the life of the bath when the pH fluctuation was greatest the Si concentration also fluctuated substantially. In fact, prior to the first KOH add back, the pH dipped to 9.39 and the Si concentration dropped close to the process control limit. This behavior is consistent with the lab study prediction of the dependency of the SM concentration on pH. Eventually, the Si concentration stabilized concurrent with pH.



**Figure 14. Si Concentration and pH versus Full-Scale System Bath Life**

### Surfactant Concentrations

The plot of the wash solution surfactant concentrations vs. bath life shows stable behavior of the anionic surfactant (D-8 and D-22) concentrations (Figure 15). Apparently, these constituents are thermally stable and unaffected by pH fluctuation. The nonionic surfactant (D-26 and D-30) concentrations fluctuated to a greater degree over the life of the bath. This outcome may be due to poor sampling methods. These nonionic surfactants enable the low foaming behavior by a reverse solubility mechanism. This mechanism causes the nonionic surfactants to go out of solution at higher temperatures ( $> 110^{\circ}\text{F}$ ). Therefore, it is crucial to operate the equipment for an extended period of time to ensure sampling of homogeneous wash solution.

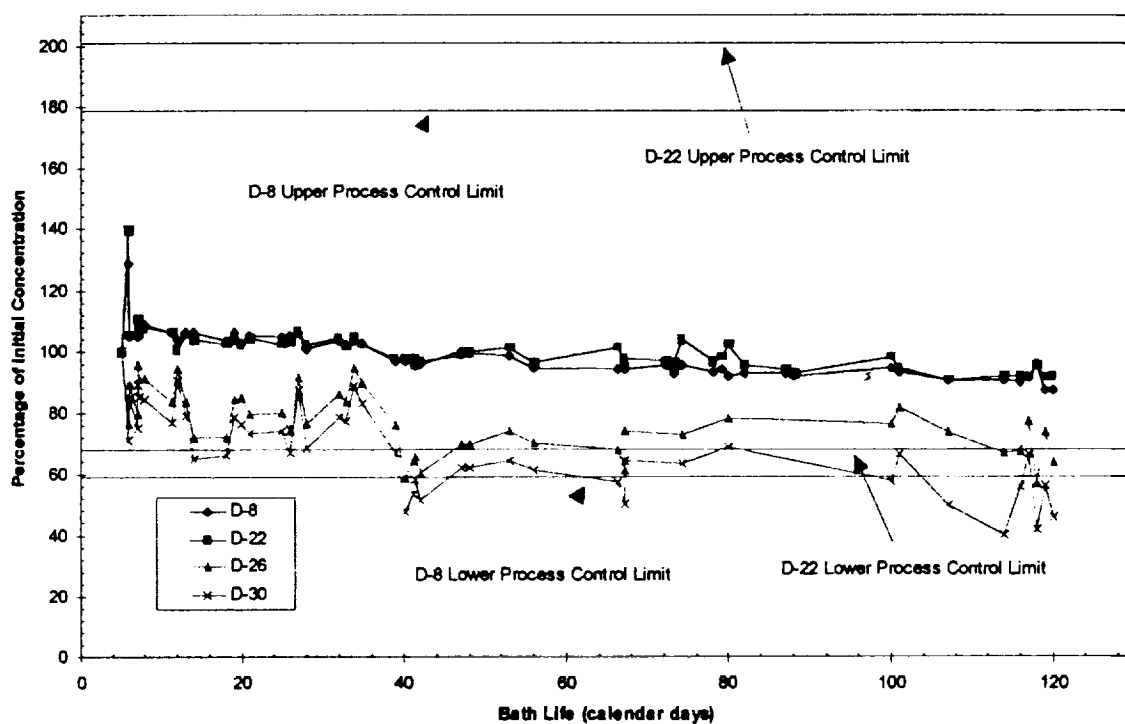
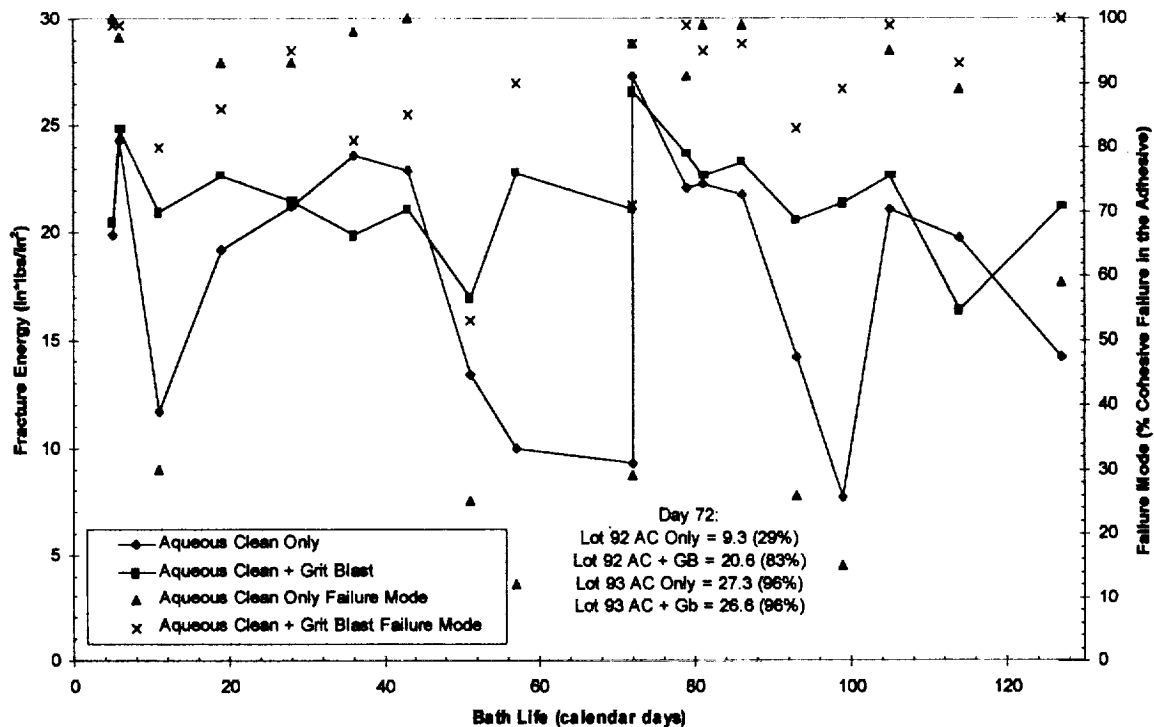


Figure 15. Surfactant Concentrations versus Full-Scale System Bath Life

## Fracture Energy

The fracture energy data (aluminum/EA 913NA adhesive) are plotted in Figure 16. Fracture energy testing is sensitive to surface phenomena which affect bond strength and failure mode. Therefore, this method is effective in differentiating potential effects of wash and rinse residues on cleaning efficiency. After 57 days of bath life, the shelf-life of the lot of EA 913NA adhesive expired. Consequently, another accepted lot was introduced into the testing. In an attempt to deconfound the effect of adhesive lot switch over, double batches of specimens were cleaned, bonded, and tested as identified in the figure.



**Figure 16. Fracture Energy (Aluminum/EA 913 NA Adhesive) versus Full-Scale System Bath Life**

The aluminum fracture energy data (aqueous clean only) show considerable fluctuation throughout bath life. After about ten days the fracture energy dropped then recovered in subsequent sample sets. Apparently, this data point was an outlier and the cause is unknown. After about 40 days of bath life, the fracture energy began gradually declining to its lowest level at about 72 days into the bath life.

This trend corresponded to two events: (1) adhesive lot switch over and (2) increasing rinse water conductivity, which corresponds to decreasing purity. The duplicate tests showed a significant discrepancy in fracture energy due to the adhesive lot change. However, these sample sets were also rinsed with low purity rinse water. After about 100 days of bath life, the fracture energy of specimens prepared with the new adhesive lot decreased to a low level. This outcome also coincides with low purity rinse water. Apparently, there was a synergistic effect on the fracture energy caused by elapsing adhesive shelf life and lower rinse water purity. Regardless, these low values were not associated with the effects on the wash solution from KOH add back chemistry. (The steel fracture energy data did not vary as much as the aluminum data which was predictable because steel is less sensitive to surface phenomena. However, the steel fracture energy vs. bath life correlation mirrored the aluminum data.)

It is crucial to note that the gritblast step offset possible effects from ineffective rinsing because the fracture energy stabilized considerably after gritblast. These values are representative of the production surface preparation process which was designed with inherent redundancy to achieve exceptional bondline surface preparation. In this case, gritblasting compensated for a deficiency in the aqueous cleaning process (poor rinsing).

#### **Conclusions of the KOH Add Back Study in the Full-Scale System**

The chemistry properties of the wash solution in the full-scale system responded as predicted by the laboratory studies. Also, the KOH add back method effectively controlled the SM concentrations and pH in the full-scale system without negatively affecting the cleaning effectiveness of the wash solution. In addition, control of the wash solution pH through KOH add back extended the bath life to at least 120 days.

#### **ACKNOWLEDGMENTS**

The authors of this paper wish to thank NASA and Thiokol RSRM Program Management and Engineering for their funding and sponsorship of this study.

#### **REFERENCES**

1. Kirk-Othmer, Encyclopedia of Technology, Vol. 17, Pages 452 - 453, Wiley, New York, 1991.
2. Zinder, B; Hertz, J; Oswald, H. R., Water Res., 1984, Vol. 18, No. 5, Pages 509 - 5112.
3. Wilhelm, E., The Physical Chemistry of the Silicates, University of Chicago Press, Chicago, 1954.